

High-molecular weight non-ionic surfactants comprising anionic terminal end groups

Summary of the invention

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The present invention relates to high-molecular weight non-ionic surfactants comprising terminal anionic end groups or a salt thereof. The present invention also relates to a process for the preparation of high-molecular weight non-ionic surfactants comprising terminal anionic end groups or a salt thereof, and the use of these high-molecular weight non-ionic surfactants comprising terminal anionic end groups as anti-scalants, surfactants and water softening agents. More in particular, the present invention relates to high-molecular ethylene oxide propylene oxide block copolymers comprising terminal anionic end groups or a salt thereof, preferably terminal carboxylate end groups or salt thereof.

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Background of the invention

Divalent cations like Ca^{2+} , Mg^{2+} and Ba^{2+} are often denoted as water hardeners as they form salts with various anions like SO_4^{2-} , CO_3^{2-} and OH^- that have a low solubility in water with the consequence that these salts precipitate. These precipitates are undesired in many household and industrial applications. Examples are laundry and dish washing machines in which it causes a greyish deposit on cloth and service-ware [S.V. Vaeck, V. Merken, Tenside Detergents 18(4), 177 - 178 (1981)]. Additionally, it causes scaling on heating elements, thereby reducing heating efficiency. Also many large-scale processes suffer from the formation of scale, among others reducing heat transfer efficiency in boilers and heaters [S. Srikant et al., Engineering Failure Analysis 10(4), 491 - 501 (2003); M.A. Sohail, A.I. Mustafa, Indian J. Chem Technol. 8(3), 223 - 226 (2001); K..Y. Chang, S. Patel, Materials Performance 35(7), 48 - 53 (1996); A. Harris et al., Desalination 146(3), 325 - 340 (1974); Z. Amjad, Ultrapure 16(7), 17 - 24 (1999)]. Not only traditional processes suffer from this phenomenon, it also hampers the introduction of new technologies, e.g. the application of membrane technology for the production of potable water [S.F.E. Boerlage et al., J. Membrane Sci. 197, 251 - 268 (2002)].

The current technology to co-ordinate (or bind; both terms are used in this patent application interchangeably) divalent cations commonly involves the use of ion exchange resins [L. Harju, T. Krook, *Talanta* **42**, 431 - 416 (1995); S.T. Iyer et al., *Reactive and Functional Polymers* **29**, 51 - 57 (1996)] or chemical anti-scalants [M. Al-Shammir et al., *Desalination* **128**, 1 - 16 (2000); S.F.E. Boerlage et al., *J. Membrane Sci.* **197**, 251 - 268 (2002); P.A.C. Bonn   et al., *Desalination* **132**, 109 - 199 (2000)]. However, the use of ion exchange resins have the disadvantage that they must be regenerated by consecutive washing steps with acid and base, thus leading to the production of substantial amounts of waste salts [W.H. Holl, *Vom Wasser* **89**, 13 - 24 (1997); X. Zhao et al., *Waterresearch* **36**(4), 851 - 858 (2002)]. Alternatively, chemical anti-scalants can be used that strongly bind cations. But also the use of these materials is disadvantageous since they must be discarded after a single use, thus creating a substantial environmental burden seen the scale of the processes involved.

Contrary to most ionic surfactants, non-ionic polymeric surfactants can be dissolved in water in high concentrations in the presence of divalent cations. A characteristic feature of many of these surfactants is the occurrence of a critical micellisation temperature (CMT), below which the surfactants are present as free molecules. Above the CMT various well-defined self-assembly structures are formed, which can be typified as micelles or more complex aggregates like rods and discs [P. Alexandridis, T.A. Hatton, *Colloids and Surfaces* **96**, 1 - 46 (1995); P. Alexandridis et al., *Macromolecules* **27**, 2414 - 2425 (1994); J.H. Mu, G.Z. Li, *Chemical Physics Letters* **345**, 100 - 104 (2001)] in which the lyophobic segments (often propylene oxide) form a core surrounded by a shell of highly solvated lyophilic segments (often ethylene oxide) that extend into the continuous aqueous phase. The core regions of such micelles have been used to emulsify otherwise insoluble material into a microphase-separated environment within a preferred continuous solvent phase [P. Alexandridis, T.A. Hatton, *Colloids and Surfaces* **96**, 1 - 46 (1995); P.R. Desai et al., *Colloids and Surfaces A* **178**, 57 - 69 (2001); P.J. Lebens, J.F.T. Keurentjes, *Ind. Eng. Chem. Res.* **35**, 3415 - 3421 (1996); R. Nagarajan, *Langmuir* **2**, 210 - 215 (1986)].

It is also known in the art to employ in detergent formulations non-ionic polymeric surfactants comprising anionic groups. For example, US 4.745.162 which is incorporated by reference herein for the US patent practice, discloses anionic poly(alkylene carbonate) polyahls having terminal acidic groups that are prepared by

converting a hydroxy terminated non-ionic polymer with cyclic or linear acid anhydrides, acid halides and the like, the hydroxy terminated non-ionic polymer being preferably be selected by the group consisting of (1) adducts of (a) monofunctional alcohols, carboxylic acids, mercaptans, primary or second amines, C₃-C₂₄ alkyl substituted phenols or C₂-C₅₀ alkoxylates thereof, and (b) either alkylene carbonates, alkylene oxides and CO₂, a mixture of alkylene carbonates, alkylene oxides and CO₂ or poly(alkylene carbonate) polyahls with (2) materials capable of reacting with the adducts to add an acidic end group thereto.

US 5.733.856, incorporated by reference herein for the US patent practice, discloses laundry detergency boosting polymer blend additives comprising (a) a polyalkylene oxide grafted with vinyl ester such as vinyl acetate and (b) a polycarboxylate, said polycarboxylate being a copolymer of acrylic acid and maleic acid or a polyacrylic acid.

US 6.100.372, incorporated by reference herein for the US patent practice, discloses polymers that are prepared by co-polymerising carbon dioxide, an alkylene oxide, preferably ethylene oxide, and a monocarboxylic chain terminator, said polymers being characterised by the formula:



wherein R is an alkyl group containing about 8 to 18 carbon atoms, R' is an alkylene group containing 2 to 3 carbon atoms, m and n range from 1 to about 30 and x ranges from 1 to about 30.

US 2001/0035271, incorporated by reference herein for the US patent practice, discloses a process for inhibiting calcium carbonate scaling in aqueous systems by adding to said aqueous systems a polymer comprising 1,2-dihydroxy-3-butene monomer units and at least a monomer derived from the group consisting of maleic acid, acrylic acid, acryl amide, methacrylic acid, itaconic acid, vinyl sulfonic acid, styrene sulfonic acid, N-t-butylacryl amide, butoxymethylacrylamide, N,N-dimethylacrylamide, sodium acrylamidomethyl propane sulfonic acid, and salts thereof, with the proviso that said polymers does not include the monomer unit $-(CH_2-CH=CH-CH_2-O)-$.

Although the polymers disclosed in US 4.745.162, US 5.733.856, US 6.100.372 and US 2001/0035271 are capable of binding cations, they lack, however, thermo-reversible properties and do not show a critical micellisation temperature (CMT) in a temperature range of practical interest (e.g. below about -40°C or above about 200°C).

5 US 3.507.721, incorporated by reference herein for the US patent practice, discloses polymers that are prepared from PEO-PPO-PEO polymers having terminal hydroxy groups and dicarboxylic acids. These polymers which do not have anionic groups are used as binders in nitrate ester plasticized propellants.

10 US 4.028.283, incorporated by reference herein for the US patent practice, discloses a process for the preparation of a non-ionic polymer from a polyalkylene glycol, e.g. a PEO-PPO-PEO block polymer having terminal hydroxyl groups, and a dicarboxylic acid anhydride, e.g. phthalic anhydride. The non-ionic polymer is used as an anti-caking agent in granular or powdery detergent compositions.

15 US 5.501.769, incorporated by reference herein for the US patent practice, discloses a Kraft-process for cooking wood wherein the wood is contacted with a composition comprising a fatty acid ester of a polyoxyalkylene glycol.

It is an object of the invention to provide high molecular weight non-ionic surfactants comprising terminal anionic end groups or salts thereof, preferably terminal carboxylate or sulphonate groups or salts thereof, more preferably terminal carboxylate groups or salts thereof.

20 It is a further object of the invention to provide high molecular weight non-ionic surfactants comprising terminal anionic end groups or salts thereof that are capable of displaying a critical micellisation temperature (CMT) of about 0° to about 200°C.

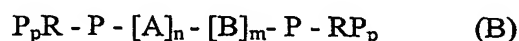
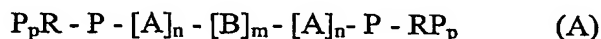
It is another object of the invention to provide high molecular weight non-ionic surfactants comprising terminal anionic end groups or salts thereof that above the CMT are capable of substantial co-ordination of divalent cations whereas below the CMT such co-ordination is substantially absent.

25 It is a further object of the invention to provide a process for the removal of multivalent cations from an aqueous system, wherein said multivalent cations are thermo-reversibly bonded to a high molecular weight non-ionic surfactant comprising anionic terminal end groups.

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Summary of the invention

According to the invention, there is provided a high molecular weight non-ionic surfactant comprising anionic groups or salts thereof, preferably terminal anionic groups and salts thereof, according to formula A or B:



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wherein:

P is a mono-valent oxygen containing anionic group or a salt thereof selected from the group consisting of oxides of carbon, sulphur and phosphorus;

15 p is in the range of 1 to 4;

R is a linear or branched, saturated or unsaturated C₂ - C₁₂ alkylene group;

A is ethylene oxide;

B is propylene oxide;

n is in the range of 5 to 1000; and

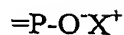
20 m is in the range of 5 to 1000.

Detailed description of the invention

According to the invention, the high molecular weight non-ionic surfactant comprising anionic groups or salts thereof according to formula A are preferred.

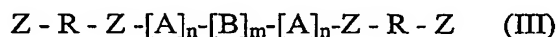
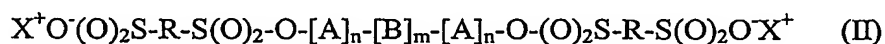
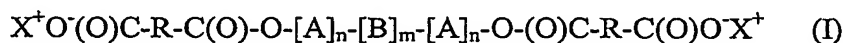
According to the invention, the oxides of carbon, sulphur and phosphorus are preferably selected from:

- C(O)O⁻X⁺ (carboxylate);
- 30 -S(O)_q-O⁻X⁺ wherein q is 1 or 2 (sulphinate and sulphonate);
- P(O)(O-X⁺)_q wherein q is 1 or 2 (phosphinate and phosphonate);
- P(O)(H)(O⁻X⁺) (phosphinate)
- =P(O)-O⁻X⁺; and



wherein X is independently hydrogen or an alkali metal, preferably lithium, sodium or potassium, or an ammonium group NR'_4^+ wherein R' is independently selected from hydrogen or linear or branched C₁-C₄ alkyl groups, or two X's are an alkaline earth metal, preferably magnesium or calcium.

According to a first preferred embodiment of the present invention, there is provided a high molecular weight non-ionic surfactant comprising terminal anionic end groups or salts thereof, said surfactant being characterised by the following general formula (I) or (II) or (III):



wherein:

X is independently hydrogen or an alkali metal, preferably lithium, sodium or potassium, or an ammonium group NR'_4^+ wherein R' is independently selected from hydrogen or linear or branched C₁-C₄ alkyl groups, or two X's are an alkaline earth metal, preferably magnesium or calcium;

R is a linear or branched, saturated or unsaturated C₂ - C₁₂ alkylene group;

A is ethylene oxide;

B is propylene oxide;

n is in the range of 5 to 1000;

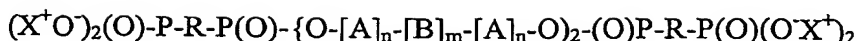
m is in the range of 5 to 1000;

q is 1 or 2; and

wherein Z is independently selected from phosphonate or phosphinate.

As will be apparent to the person skilled in the art, formula (III) allows for the structures of the type:





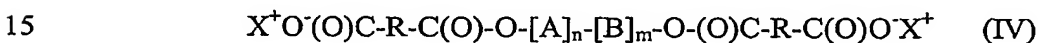
and the like, i.e. including polymeric type structures.

According to the invention, X is preferably hydrogen or an alkali metal,
5 preferably sodium or potassium.

R is preferably a linear and saturated alkylene group, preferably a linear and saturated C₂ - C₆ alkylene group and preferably an ethylene group.

Preferably, n is in the range of 10 to 100. It is also preferred that m is in the range of 10 to 100.

10 According to a second preferred embodiment of the present invention, there is provided a high molecular weight non-ionic surfactant comprising terminal anionic end groups or salts thereof, said surfactant being characterised by the following general formula (IV) or (V) or (VI):



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wherein:

X, R, A, B, n, m, q and Z are as defined for formula (I), (II) and (III).

According to the invention, the high molecular weight non-ionic surfactant comprising terminal anionic end groups or salts thereof which are characterised by the
25 general formula (I) or (II) or (III) are most preferred.

The present invention also relates to a process for the preparation of a high molecular weight non-ionic surfactant comprising terminal anionic end groups or salts thereof, wherein a hydroxy terminated ethylene oxide propylene oxide triblock copolymer according to formula (VII) or formula (VIII):

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is reacted with a compound according to formula (IX):



- 5 wherein P is a mono-valent oxygen containing anionic group or a salt thereof selected from the group consisting of oxides of carbon, sulphur and phosphorus;
p is in the range of 1 to 4. According to the invention, the oxides of carbon, sulphur and phosphorus are preferably selected from

- 10 -C(O)OY;
-S(O)_q-OY;
-P(O)(OY)_q wherein q is 1 or 2; and
-P(O)(H)(OY)
=P(O)-OY and
15 =POY

- wherein Y is independently hydrogen, a halogen, a linear, cyclic or branched, saturated or unsaturated C₁ - C₁₂ alkyl group, a optionally substituted C₆ - C₁₂ aralkyl group, preferably a optionally substituted benzyl group, an optionally substituted C₆ - C₁₂
20 alkaryl group, preferably an optionally substituted phenyl group, or an alkaline or alkaline earth metal cation.

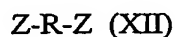
A group like =P(O)-OY means that two groups R are bonded to the same phosphorus atom as will be apparent to the skilled person..

- According to a preferred embodiment of the invention, the groups P are terminal
25 mono-valent oxygen containing anionic groups or salts thereof.

More preferably, p = 1 and the diacid or a suitable derivative thereof, e.g. a dicarboxylic acid or a disulphonic acid, has the formula (X), (XI) or (XII):



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wherein in formula (X) Y is hydrogen, a halogen, a linear, cyclic or branched, saturated or unsaturated C₁ - C₁₂ alkyl group, a optionally substituted C₆ - C₁₂ aralkyl group, preferably an optionally substituted benzyl group, an optionally substituted C₆ - C₁₂ alkaryl group, preferably an optionally substituted phenyl group, or an alkaline or alkaline earth metal cation, and in formula (X) hydrogen or an alkaline or alkaline earth metal cation, or wherein the two YO moieties represent a single oxygen atom so that the dicarboxylic acid derivative of formula (X) or the disulphonic acid derivative of formula (XI) represents an anhydride, and wherein R is defined as above. In formula (XII) Z is a phosphonate group or a phosphinate group, wherein the counter-ions are most preferably are as Y in formula (VI). That means that Z can be -P(O)(OY)₂, -P(O)(OH)(OY), -P(O)(H)(OY) and the like.

According to the present invention, Y in formula (X) is preferably hydrogen, halogen or a linear, cyclic or branched, saturated or unsaturated C₁ - C₁₂ alkyl group or an alkaline or alkaline earth metal cation. More preferably, Y in formula (X) is hydrogen, a halogen or an alkaline or alkaline earth metal cation. Even more preferably, Y in formula (X) is hydrogen or a halogen, preferably chlorine or bromine. Even more preferably, the dicarboxylic acid derivative of formula (X) is a dicarboxylic anhydride, most preferably succinic anhydride. In formula (XI), Y is preferably hydrogen or an alkaline or alkaline earth metal cation. Most preferably, in formula (XI) Y is hydrogen. As said above, most preferred counter-ions present in formula (XII) are those defined for Y in formula (XI).

A suitable example of a hydroxy terminated ethylene oxide propylene oxide block copolymer is Pluronic P85 (CAS number 9003-11-6) that is available from BASF. For other suitable examples, reference is made to the following web site of BASF showing the basic Pluronic grid:

www.basf.com/static/OpenMarket/Xcelerate/Preview_cid-82931199931_pubid-974236729499_c-Article.html

The high molecular weight non-ionic surfactant comprising terminal anionic end groups or salts thereof has a CMT of about 0° to about 200°C, preferably about 25°C to about 100°C. The CMT can be adjusted by selecting a suitable block ratio of ethylene oxide and propylene oxide in the ethylene oxide propylene oxide triblock copolymer. In

general, less propylene oxide in the triblock copolymer results in higher CMT values. If the CMT is about 0°C, the high molecular weight non-ionic surfactant according to the present invention can be used under low temperature conditions, e.g. in groundwater or (sub)soil water. If the CMT is for example above 100°C, the surfactant according to the invention can be used under high temperature conditions, e.g. in industrial steam generators.

The high molecular weight non-ionic surfactant comprising terminal anionic end groups or salts thereof is capable of quantitative binding of multivalent cations, preferably divalent cations, preferably Ba^{2+} , Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Cr^{2+} , Cr^{3+} , Cr^{6+} and in particular Mg^{2+} , Ca^{2+} and Ba^{2+} , above the CMT with high affinity, whereas essentially no binding occurs below the CMT. Decreasing the temperature to values below the CMT completely liberates the bonded multivalent cations, preferably divalent cations. The selective binding of multivalent cations preferably divalent cations is important to avoid unwanted salt depositions in many processes, ranging from household applications like laundry and dish washing to large-scale processes such as steam production in boilers and the production of potable water using membrane technology.

Accordingly, the present invention also provides a process for decreasing the hardness of an aqueous system, wherein a high molecular weight non-ionic surfactant comprising terminal anionic end groups or salts thereof is added to said aqueous system.

In the present patent application, the term "aqueous system" is to be understood as to include any system comprising water, including but not limited to cooling water, boiler water, desalination, house hold apparatus such as dish washers and laundry washing machines, gas scrubbers, blast furnaces, sewage sludge thermal conditioning equipment, membrane processes, paper processing, mining circuits and the like, as will be apparent to the person skilled in the art. Membrane processes may comprise e.g. reverse osmosis, nanofiltration, ultrafiltration, microfiltration, membrane distillation, electrodialysis, etc. In particular, the term "aqueous system" is to be understood as systems comprising water such as dish washers and washing machines.

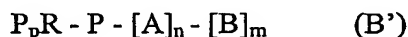
The high molecular weight non-ionic surfactant comprising terminal anionic end groups or salts thereof according to the invention are in particular suitable for use as anti-scalant, in processes for the desalination or softening of water and the removal of

heavy metals, that is multivalent metal cations, preferably divalent metal cations, from aqueous systems contaminated with such metals and in industrial and domestic wash processes and products used for such processes.

According to the present invention, a multivalent metal cation is any metal cation
 5 that has an oxidation state of at least 2 or higher, preferably an oxidation state of at least 2 to 6.

The present invention also relates to a process for the removal of multivalent metal cations from an aqueous system, wherein said multivalent metal cations are contacted with and thermo-reversibly bonded to a high molecular weight non-ionic
 10 surfactant comprising anionic terminal end groups. That is, that at higher temperatures the multivalent metal cations are bonded to the high molecular weight non-ionic surfactant comprising terminal anionic end groups or salts thereof, and that the multivalent metal cations are released from said high molecular weight non-ionic surfactant comprising terminal anionic end groups or salts thereof at lower
 15 temperatures. The present invention relates therefore in particular to a process for the removal of multivalent metal cations from an aqueous system, wherein said multivalent metal cations are contacted at a first temperature with and thermo-reversibly bonded to a high molecular weight non-ionic surfactant comprising anionic terminal end groups or salts thereof to form a cation-surfactant complex, and wherein said cation-surfactant
 20 complex is subjected to a second temperature, the second temperature being lower than the first temperature, to release said multivalent metal cations from said high molecular weight non-ionic surfactant comprising terminal anionic end groups or salts thereof. Non-metal multivalent cations may also be removed.

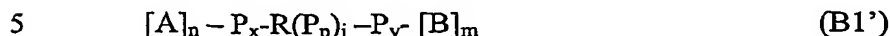
According to another embodiment of the invention, there is provided a surfactant
 25 having the following formula:



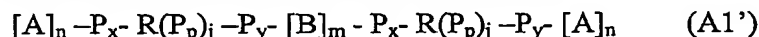
with A, B, R, P, n and m as defined above, with generally $[B]_m$ having a terminal OH group.

Although the description and formulas generally refer to terminal end groups, the
 30 invention is not limited to the compounds of the invention comprising anionic groups or salts thereof as terminal end groups as described in preferred embodiments having formula's A, B or B'. The invention is also directed to surfactants according to the invention comprising non-terminal end groups, or surfactants according to the

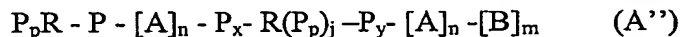
invention comprising both non-terminal and terminal end groups, as will be clear to the person skilled in the art. In an embodiment, such surfactant is described by the following formula:



with A, B, R, P, n and m as defined above, wherein x, y are 0 or 1 and wherein $x+y=1$ or 2; j is 1 or 2, i.e. 1 or 2 P_p groups like e.g. $-C(O)O^-X^+$ (carboxylate); $-S(O)_q-O^-X^+$ wherein q is 1 or 2 (sulphinate and sulphonate); $-P(O)(O^-X^+)_q$ wherein q is 1 or 2 (phosphinate and phosphonate); $-P(O)(H)(O^-X^+)$ (phosphinate); $=P(O)-O^-X^+$; and $=P-O^-X^+$. Preferably, $y = 1$. The person skilled in the art will understand that in formula A1 also two non-terminal groups may be present, i.e.:

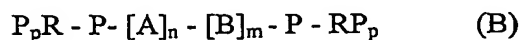
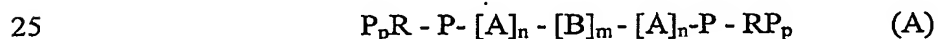


In yet another embodiment, the surfactant has a structure according to:



15 Wherein P, p, A, n, x, R, j, y, B are as described above. It will be clear to the person skilled in the art that other permutation are also possible.

Further, the invention is not limited to only multivalent metal cations. Hence, in an embodiment there is provided a process for the removal of multivalent cations, e.g. comprising, organic multivalent cations, from an aqueous system, wherein said aqueous system is treated with a high molecular weight non-ionic surfactant comprising anionic groups or salts thereof, preferably terminal anionic groups and salts thereof, wherein said high molecular weight non-ionic surfactant comprising anionic groups or salts thereof is represented by formula A or formula B:



wherein:

30 P is a mono-valent oxygen containing anionic group or a salt thereof selected from the group consisting of oxides of carbon, sulphur and phosphorus;
p is in the range of 1 to 4;
R is a linear or branched, saturated or unsaturated $C_2 - C_{12}$ alkylene group;

A is ethylene oxide;
B is propylene oxide;
n is in the range of 5 to 1000; and
m is in the range of 5 to 1000.

- 5 Further, in an embodiment, the process of the invention may also apply surfactants according to formula's B', A1, A1', A'', and B1'.

Example 1

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Pluronic P85 (50 g) was purified by dissolving it in diethyl ether (200 g) resulting into the formation of a cloudy solution. The solution was clarified by sedimentation in a laboratory centrifuge (3000 r.p.m., 30 minutes). The clarified solution was slowly added to cold (5°C) pentane under continuous stirring thereby forming a precipitate.
15 The precipitate was isolated by filtration (Büchner) and dried under vacuum. Succinic anhydride was recrystallised from dichloromethane/hexane.

- Purified Pluronic P85 (16.8 mmol of terminal OH groups, 40 g) was dissolved in toluene (160 ml), followed by the addition of recrystallised succinic anhydride (50.4 mmol, 5.04.g). The reaction is performed for 2 hours at 90°C and 2 hours at 100°C,
20 respectively, during which the water formed is removed by azeotropic distillation by means of a Dean-Stark trap. After the reaction was completed, the solvent is evaporated leaving an oily product which was dissolved in water. Thereafter, Na₂CO₃ was added in small portions until CO₂ was formed; the final pH of the solution was about 11 - 12. After about one hour, the solution was acidified by adding diluted sulphuric acid until
25 the pH was about 1 - 2. Then, sodium sulphate was added until saturation. The product was subsequently extracted three times with butanol. The organic phase was washed with saturated sodium sulphate and dried (anhydrous Na₂SO₄, 5°C, o/n). Butanol was evaporated and the product was re-dissolved in diethyl ether to form an about 10% solution, followed by sedimentation. The clear solution was concentrated to about 30%
30 and precipitation was induced with an equal volume of pentane. The final product is obtained after filtration and drying under vacuum at room temperature. The product had an average molecular weight of 4745 g/mol as determined by SEC. The

amount of carboxylic groups was determined by potentiometric titration; the titration curves showed a pKa value of 4.67.

Example 2

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In this example, the temperature-induced aggregation behaviour to create thermo-reversible ion binding in the aqueous shell of the polymer according to Example 1 is demonstrated.

Differential scanning calorimetry experiments (1 % by weight solution in water, 10°/min) demonstrated that the polymer according to Example 1 had a critical micelle formation temperature (CMT) of around 32°C at low ionic strength (i.e. no salt added), a value that decreases to about 26°C at an ionic strength of 1000 mmol/L. The presence of the carboxylic groups lowers the CMT by approximately 2°C, since Pluronic P85 displays a CMT of 34°C at low ionic strength, a value decreasing to about 28°C at 1000 mmol/L.

The calorimetry titration experiments were performed by using a MicroCal VP-ITC apparatus with a cell volume of 1.4431 mL, adding 70 injections of 4 µL of a CaCl₂ solution (30.0*10⁻³ mol/L) to a x wt% solution of polyacrylic acid (a) and a 1 wt% solution of the polymer according to Example 1 (b) at 25 and 50 °C; concentrations were chosen such that both solutions contained an equal number of carboxylic groups.

Isothermal Titration Calorimetry (ITC) has proven to be an effective method to evaluate the heat effects occurring upon aggregation and ion binding and release [T. Christensen et al., J. Am Chem Soc. **125**, 7357 - 7366 (2003)]. Initially, ITC experiments have been performed to characterise the binding of Ca²⁺ to poly acrylic acid (PAA; Figure 1). PAA is known to be able to bind divalent cations without the formation of micelles [J. Pochard et al, Colloid Polym. Sci. **276**, 1088 (1998)]. The Ca²⁺ ions are bonded by two acid groups on the same PAA molecule. From Figure 1 the corresponding enthalpy of bonding can be deduced and equals 23.8 kJ/mol Ca²⁺. The binding capacity of PAA for Ca²⁺ equals the total of charges available on the PAA and from the measurements an affinity constant, defined as $-\log \frac{[\text{COO}_2\text{Ca}]}{[\text{Ca}^{2+}][\text{COO}^-]^2}$ of 4.55 can be deduced, a value in close agreement with literature data [J. Pochard et al, Colloid Polym. Sci. **276**, 1088 (1998)].

Reference experiments were performed to verify the occurrence of any binding to Pluronic P85, both below and above its CMT. However, it appeared that no noticeable binding to P85 occurred.

ITC experiments at $\text{pH} > 5$ with Ca^{2+} , the Pluronic P85 and the polymer according to Example 1 (CAE-85) yielded the results shown in Figure 4 for temperatures below (25°C) and above (50°C) CMT. From figure 4, it can be seen that no significant binding of Ca^{2+} to Pluronic P85 occurs at either temperature and for the polymer according to Example 1 at 25°C. Binding of Ca^{2+} only occurs to the polymer according to Example 1 at 50°C. S2 and CAE-85 refer to the carboxylate modified Pluronic P85, the polymer of example 1.

Performing ITC experiments at $\text{pH} > 5$ with Ca^{2+} and the polymer according to Example 1 yielded the results shown in Figure 1 for temperatures below (25°C) and above (50°C) CMT, respectively. From Figure 1, it can be seen that no significant binding to the polymer according to Example 1 occurred when the surfactant molecules are freely dissolved in solution. However, Ca^{2+} strongly bonded to the polymer according to Example 1 when it was present in a micellar form.

The binding capacity is approximately 1.5 times the available number of acid groups which, without being bound by theory, suggests a different binding mechanism as compared to PAA. Without being bound by theory, the binding of Ca^{2+} to aggregates of the polymer according to Example 1 is caused by a charge compensation mechanism, rather than direct 1:2 binding, similar to the behaviour of common ionic surfactants. The binding of Ca^{2+} ions to the polymer according to Example 1 can be described with a single-site binding model with a binding constant of 2.83, a value somewhat lower than found for the binding to PAA. For the polymer according to Example 1, the enthalpic effect equals 71.7 kJ/mol Ca^{2+} , about 3 times the value for binding to PAA. This indicates that, without being bound by theory, binding of Ca^{2+} also causes a substantial structural change in the micellar shell. In addition to the experiments with Ca^{2+} ions, similar results have been obtained using Ba^{2+} (see Table 1).

Table 1

Enthalpic (ΔH , kJ/mol) and entropic (ΔS , $\text{kJ}/(\text{mol} \cdot ^\circ\text{C})$) contribution to the binding of Ca^{2+} , Zn^{2+} , La^{3+} and Ba^{2+} to PAA and the polymer according to Example 1, respectively. Also the binding constants (pK_c) are given.

	<i>Ca</i>	<i>Zn</i>	<i>La</i>	<i>Ba</i>
$\Delta H_{\text{PAA}, T=50^\circ\text{C}}$	$25.5 \pm 0.4 \cdot 10^3$			$26.6 \pm 0.7 \cdot 10^3$
$\Delta H_{\text{Ex. 1}, T=50^\circ\text{C}}$	$46.6 \pm 1.1 \cdot 10^3$	$85.3 \cdot 10^3$	$4276 \cdot 10^1$	$64.5 \pm 0.7 \cdot 10^3$
$\Delta S_{\text{PAA}, T=50^\circ\text{C}}$	164.22			159.13
$\Delta S_{\text{Ex. 1}, T=50^\circ\text{C}}$	203.89	323.76	13284.20	254.60
$\text{pK}_c_{\text{PAA}, T=50^\circ\text{C}}$	4.55			4.02
$\text{pK}_c_{\text{Ex. 1}, T=50^\circ\text{C}}$	3.11	3.13	2.86	2.87

Example 3

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To verify the reversibility of the metal ion binding to CAE-85 micelles and to demonstrate that the surfactants can be regenerated a continuous membrane filtration experiment has been performed in complete recycle mode. System volume is about 2 dm^3 . Cross flow is 150 l/h. Pressure is 20 psi. Surfactant concentration is 0.5 wt.%. In this experiment, a temperature cycle was applied while a solution of CAE-85 and CaCl_2 was led through the flat membrane with a cut-off value of 3 kDa (membrane area $6.545 \cdot 10^{-3} \text{ m}^2$). The calcium concentration at the permeate side of the membrane was measured by colorimetric titration. The membrane retains the CAE-85 surfactant molecules, whereas the Ca^{2+} cations can permeate through the membrane. During the experiment, the temperature of the solution is increased from 20°C (below CMT) to 50°C (above CMT) and again decreased to 20°C . Each temperature was maintained for at least one hour, in which a steady state Ca^{2+} flux through the membrane was obtained. Below the CMT, the Ca^{2+} concentration in the permeate stream equals the feed concentration and increasing the temperature above the CMT reduces the amount of free calcium in the system. A lower Ca^{2+} permeate concentration is measured, equal to 80% of the maximum binding capacity of the micellized surfactant present. By

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lowering the temperature to 20°C, the Ca^{2+} concentration in the permeate stream becomes again equal to the feed concentration, confirming the complete release of all the bound Ca^{2+} ions.

5 Example 4

ITC experiments at $\text{pH} > 5$ with different cations (Na^+ , Ca^{2+} , Ba^{2+} , Mg^{2+} , Zn^{2+} , Cu^{2+} and La^{3+}) and the polymer according to Example 1 yielded the results shown in Figure 3 for temperatures above (50°C) CMT. From Figure 3, it can be seen that no significant binding to the polymer according to Example 1 occurred for monovalent cations, while multivalent cations strongly bonded to the polymer according to Example 1.

Example 5

Self-consistent field theory modelling calculations were made in which the fractional distribution of PPO, PEO, solvent, Na^+ and Cl^- as a function of distance (expressed as number of equally sized layers) from the core of the micel are made for the following conditions: added NaCl 10^{-4} M, pH 8.5 and micellar state. Two positions of the carboxylate group in the surfactant were examined: P1: the carboxylate group is at the terminal end, representative for the polymer of Example 1, and P2: the carboxylate group is located between the PPO and PEO blocks. From Figure 2, it can be seen that PPO, PEO, solvent and Cl^- distribution are similar for the P1 and P2. The fractional distribution of Na^+ is slightly different. P2 shows a higher and sharper Na^+ distribution than P1. Despite these differences, the effect of a charge compensation mechanism is apparent for P2 and P1. Therefore it can be concluded that P2 will show similar multivalent ion binding capabilities as P1. For the sake of simplicity, the alkyl groups R have not been added in the schematic description of P1 and P2, as indicated in figure 2. P1 is an example of the surfactant of the invention having terminal anionic groups; P2 is an example of a surfactant having non-terminal anionic groups.